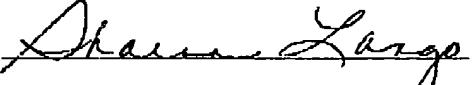
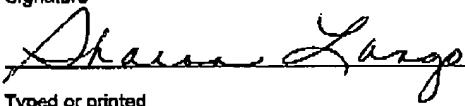


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on February 28, 2005		For: ALKALI/TRANSITION METAL HALO- AND HYDROXY-PHOSPHATES AND RELATED ELECTRODE ACTIVE MATERIALS	
Signature 		Art Unit 1745 Examiner Chaney, C.	
Typed or printed name Sharon Lango			
<p>This Appeal Brief is being transmitted in furtherance of the Notice of Appeal filed on <u>December 31, 2004</u>. The Appeal Brief (27 pages, including Appendices), is attached.</p> <p>The fee for transmitting this Appeal Brief is (37 CFR 41.20(b)(2)) <u>\$600.00</u></p> <p> <input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. Therefore, the fee shown above is reduced by half, and the resulting fee is: <u>\$300.00</u> <input type="checkbox"/> A check in the amount of the fee is enclosed. <input type="checkbox"/> Payment by credit card. Form PTO-2038 is attached. <input type="checkbox"/> The Director has already been authorized to charge fees in this application to a Deposit Account. I have enclosed a duplicate copy of this sheet. <input checked="" type="checkbox"/> The Director is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. <u>220100</u>. I have enclosed a duplicate copy of this sheet. <input type="checkbox"/> A petition for an extension of time under 37 CFR 1.136(a) (PTO/SB/22) is enclosed. </p> <p>WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.</p> <p>I am the  <input type="checkbox"/> applicant/inventor <input type="checkbox"/> assignee of record of the entire interest. See 37 CFR 3.71. See 37 CFR 3.71. Statement under 37 CFR 3.73(b) is enclosed. <input checked="" type="checkbox"/> attorney or agent of record. Registration Number 45,057. <input type="checkbox"/> attorney or agent under 37 CFR 1.34(a). Registration number if acting under 37 CFR 1.34(a) <u> </u></p> <p>Michael Ross Typed or Printed Name</p> <p>702-558-1000 Telephone Number</p> <p>February 28, 2005 Date</p> <p>NOTE: Signatures of all the inventors or assignees of record of the entire interest or their representative(s) are required. Submit multiple forms if more than one signature is required, see below.</p> <p><input checked="" type="checkbox"/> Total of 2 forms are submitted.</p>			

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		Art Unit 1745	Examiner Chaney, C.		
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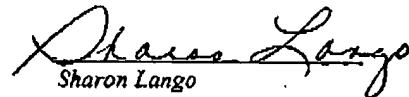
IN THE UNITED STATES PATENT & TRADEMARK OFFICE

Application No.: 10/045,685

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Filing Date: 11/7/2001

Applicant: Barker et al.


Sharon Lango

Group Art Unit: 1745

Examiner: Chaney, C.

Title: **ALKALI/TRANSITION METAL HALO- AND
HYDROXY-PHOSPHATES AND RELATED
ELECTRODE ACTIVE MATERIALS**

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APPEAL BRIEF UNDER 37 C.F.R. §41.37

If any charges or fees must be paid in connection with the following communication, they may be paid out of our Deposit Account No. 220100.

This Appeal Brief Under 37 C.F.R. §41.37 is in furtherance of Appellants' Notice of Appeal filed on December 31, 2004, which was filed in response to the final Office Action mailed November 2, 2004, Paper No. 20041101.

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1. REAL PARTY OF INTEREST

Valence Technology, Inc., a Delaware corporation, is the real party of interest in the present Appeal. Valence Technology, Inc. is the owner of the present Application by way of an assignment from Applicants Jeremy Barker, M. Yazid Saidi and Jeffrey Swoyer, recorded May 30, 2002 at reel no. 012942, frame no. 0953.

2. RELATED APPEALS AND INTERFERENCES

There is currently no other related appeal or interference pending before the Board, which would affect or be affected by or have a bearing on the Board's decision in this Appeal.

3. STATUS OF CLAIMS

A. Claims 1 - 100 have been cancelled, and Claims 101 - 153 are currently pending.

B. Claims 101 - 109, 116 - 134 and 141 - 153 currently stand rejected under 35 U.S.C. §102(b) as being anticipated by U.S. Patent No. 5,721,070 to Shackle ("Shackle 070").

C. Claims 110 - 115 and 135 - 140 are objected to as being dependent upon a rejected base Claim, and were deemed allowable if rewritten in independent form. Thus, Claims 110 - 115 and 135 - 140 form no part of this Appeal.

4. STATUS OF AMENDMENTS

All Claim amendments have been entered and considered by the Examiner.

5. SUMMARY OF THE CLAIMED SUBJECT MATTER

The present invention is directed to a novel electrode active material (independent Claim 101), as well as batteries (independent Claim 126) containing the same. The electrode active material is represented by the general formula:



wherein,

- (a) A is selected from the group consisting of Li, Na, K, and mixtures thereof, and $0 < a \leq 8$;
- (b) M comprises one or more metals, wherein at least one of the one or more metals is capable of undergoing oxidation to a higher valence state, and $1 \leq b \leq 3$; and
- (c) Z is selected from the group consisting of a hydroxyl, a halogen, and mixtures thereof, and $0 < d \leq 6$;

wherein A, M, Z, a, b and d are selected so as to maintain electroneutrality of the electrode active material.

6. GROUNDS OF REJECTION TO BE REVIEWED ON APPEAL

- A. Rejection of Claims 101 - 109, 116 - 134 and 141 - 153 under 35 U.S.C. §102(b) as being anticipated by U.S. Patent No. 5,721,070 to Shackle ("Shackle 070").

7. ARGUMENT

7.A. Shackle '070 Does Not Teach or Suggest the Invention Recited in Claims 101 - 109, 116 - 134 and 141 - 153

The Examiner erred in rejecting Claims 101 - 109, 116 - 134 and 141 - 153 under 35 U.S.C. §102(b), as being anticipated by U.S. Patent No. 5,721,070 to Shackle ("Shackle 070"). (See, final Office Action, paper no. 20041101, pgs. 2-3). Appellants submit that Shackle '070 does not explicitly teach the claimed subject matter. Appellants further submit that the claimed subject matter could not be *at once envisioned* by one with ordinary skill in the art, based on the teachings of Shackle '070. Accordingly, Appellants respectfully request reversal of the Examiner's rejection.

Shackle '070 discloses, among other things, an electrode material represented by the general formula (I):



wherein:

- (i) M is an alkali metal ion,
- (ii) T is a metal ion capable of existing in more than one stable oxidation state, and is selected from the group consisting of Mn, Fe, V, Ti, Co, Cu, Cr, Sn, Pb, W and Mo;
- (iii) A is a multi-element anion with a negative charge greater than 1, and is selected from the group consisting of SiO_4 , TiO_4 , VO_4 , FeO_4 , MnO_4 and PO_4 ;
- (iv) x is from about 1 to about 20;
- (v) y is from about 1 to about 4; and
- (vi) z is from about 1 to about 7.

Shackle '070 teaches that in some embodiments, the electrode material is "doped" by adding "other anions" (e.g. O^{2-} , S^{2-} , OH^- , F^- and Cl^-). (See, Col. 4, ll. 34 - 67 of Shackle '070).

In contrast, Claims 101 - 109, 116 - 134 and 141 - 153 of the present Application recite, among other things, an electrode active material represented by the general formula (II):



wherein,

- (a) A is selected from the group consisting of Li, Na, K, and mixtures thereof, and $0 < a \leq 8$;
- (b) M comprises one or more metals, wherein at least one of the one or more metals is capable of undergoing oxidation to a higher valence state, and $1 \leq b \leq 3$; and
- (c) Z is selected from the group consisting of a hydroxyl, a halogen, and mixtures thereof, and $0 < d \leq 6$;

wherein A, M, Z, a, b and d are selected so as to maintain electroneutrality of the electrode active material

Appellants respectfully submit that the electrode active materials recited in Claims 101 - 109, 116 - 134 and 141 - 153 are not anticipated by the teachings of Shackle '070.

First, Shackle '070 does not specifically recite as a subgenus, the electrode active materials represented by general formula (II). In addition, none of the individual active material compounds specifically listed in Shackle '070 fall within the genus of materials described by Appellants' general formula (II). Instead, it is necessary to pick-and-choose

from among the multitude of possible selections for the variables A, M, T, z, y and z of Shackle's general formula (I), and then "dope" into the material either a halogen or hydroxyl moiety (or mixture thereof) selected from among the "other anions" described in Shackle '070, in order to derive the specific subgenus of electrode active materials described by Appellants' general formula (II).

Furthermore, Shackle '070 fails to: (1) provide any teaching of a stoichiometric relationship between the "other anions" and the variables A, M, and T, (2) provide examples of active materials containing such "other anions," and (3) describe how to make electrode active materials "doped" with such "other anions."

Accordingly, Shackle '070 does not anticipate the claimed electrode active materials, because the claimed electrode active materials (as represented by Appellants' general formula (II)) are not explicitly taught in Shackle '070.

Second, the claimed electrode active materials could not be *at once envisaged* from the teachings of Shackle '070, by one with ordinary skill in the art. Appellants submit that Shackle's general formula (I) *embraces a vast number of electrode active materials*, not a limited number of materials which might allow one with ordinary skill in the art to *envisage* the materials recited in the present Claims.

Additionally, the Examiner has failed to demonstrate how or why one with ordinary skill in the art would *at once envisage* the claimed electrode materials based on the teachings of Shackle '070. Appellants submit that Shackle '070 fails to provide any explicit reason or benefit for selecting, among the multitude of active materials embraced Shackle's general formula (I), in combination with the teaching that (in some embodiments) the electrode material is "doped" by adding "other anions," those electrode active materials which are recited in the Claims.

Furthermore, Shackle '070 lacks any teaching which would *suggest* to one with ordinary skill in the art to pick-and-choose from among the multitude of possible selections for A, M, T, x, y and z of Shackle's general formula (I), then "dope" into the material either a halogen or hydroxyl moiety (or mixture thereof) selected from among the "other anions" described in Shackle '070, in order to arrive at the claimed electrode active materials. Appellant submits that Shackle '070 does nothing to narrow its generic teachings of electrode active materials to a number sufficiently small to support a §102(b) rejection under the rationale of In re Petering, 133 USPQ 275 (CCPA 1962), In re Schaumann, 197 USPQ 5 (CCPA 1978), and related cases.

Stated differently, Shackle '070 lacks any teaching which would motivate one with ordinary skill in the art to first substitute as a particular combination the following variables into Shackle's general formula (I), and then "dope" into the material either a halogen or hydroxyl moiety (or mixture thereof) selected from among the "other anions" described in Shackle '070:

- (1) M = Li, Na, K, or a mixture thereof,
- (2) A = PO₄,
- (3) 0 < x ≤ 8,
- (4) 1 ≤ y ≤ 3, and
- (5) z = 3.

The Examiner asserts "that the compounds A_aM_b(PO₄)₃Z_d recited by the Appellants are identical to the compounds M_xT_yA_z disclosed by Shackle for the instances where A is PO₄, one of only six anions specifically listed by Shackle as useful in his invention." (See, final Office Action, paper no. 20041101, pg. 3). Appellants respectfully traverse the Examiner's assertion.

The selection of a polyanion for moiety A of Shackles general formula (I) is *only one of many selections that must be made* in order to derive the specific subgenus of electrode active materials described by Appellants' general formula (II).

Stated differently, in addition to selecting $A = PO_4$, one with ordinary skill in the art would have to select and substitute, as a particular combination, the following *four* variables into Shackle's general formula (I), and then "dope" into the material either a halogen or hydroxyl moiety (or mixture thereof) selected from among the "other anions" described in Shackle '070:

- (1) $M = Li, Na, K$, or a mixture thereof,
- (2) $0 < x \leq 8$,
- (3) $1 \leq y \leq 3$, and
- (4) $z = 3$.

Accordingly, contrary to the Examiner's assertion that Appellants' general formula (II) can be derived from Shackle's general formula (I) by simply selecting $A = PO_4$, one must actually make selections for a total of *five* variables, and then further select and "dope" into the material one or more of the "other anions" described in Shackle '070.

The Examiner also asserts that "one with ordinary skill in the art would be familiar with compounds of the formula $M_xT_yA_z$ with $A = PO_4$ and $z = 3$ as evidenced by the publications cited in the Shackle patent." (See, final Office Action, paper no. 20041101, pg. 4). Presumably, the Examiner is referring to Yong et al., Mat. Res. Bull., vol. 25 pp. 841-844 (1990) ("the Yong reference") cited on the face of Shackle '070 and attached hereto as an Appendix. In order to support the Examiner's rejection under 35 U.S.C. §102(b), one with ordinary skill in the art must be able to *at once envisage* the claimed invention *based on the teachings of Shackle '070 alone*. Appellants submit it is improper for the Examiner to look to any reference other than Shackle '070 to support the

Examiner's assertion that the claimed electrode materials could be *envisioned* from the teachings of Shackle '070, because the Examiner is relying on 35 U.S.C. §102(b).

In addition, Appellants submit the Examiner has failed to demonstrate that there is any teaching or suggestion in either Shackle '070 or any of the references cited on the face of the Shackle '070 patent, which would motivate one with ordinary skill in the art to combine the their teachings in order to arrive at the claimed invention. In fact, although the Yong reference does teach how to make materials of the formula $MTi_2(PO_4)_3$ (M=Li, Na, K), Yong does not teach or suggest use of such materials as electrode active materials in an electrochemical cell. Yong does not support the contention that "compounds of the formula $M_xT_yA_z$ with A = PO_4 and z = 3" are well known in the art and recognized as standard in the relevant art. Accordingly, Appellants submit the Examiner's contention can not stand.

In summary, Appellants respectfully submit that the electrode active materials recited in Claims 101 - 109, 116 - 134 and 141 - 153 are not explicitly taught (as a subgenus or a species thereof) by Shackle '070, and further could not be *at once* *envisioned* by one with ordinary skill in art, based on the teachings of Shackle '070. Therefore, Appellants respectfully submit that Claims 101 - 109, 116 - 134 and 141 - 153, are patentably distinct from Shackle '070. Accordingly, Appellants respectfully request reversal of the Examiner's rejection.

8. CONCLUSION

Appellants submit the Examiner erred in rejecting Claims 101 - 109, 116 - 134 and 141 - 153 under 35 U.S.C. §102(b), as being anticipated by Shackle 070. In view of the remarks presented herein, Appellants respectfully solicit the Honorable Board to reverse the Examiner's rejection.

Respectfully submitted,



By:

Michael Ross
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APPENDIX AListing of Claims.

1-100 (CANCELLED)

101 (PREVIOUSLY PRESENTED): An electrode active material represented by the general formula:



wherein,

- (a) A is selected from the group consisting of Li, Na, K, and mixtures thereof, and $0 < a \leq 8$;
- (b) M comprises one or more metals, wherein at least one of the one or more metals is capable of undergoing oxidation to a higher valence state, and $1 \leq b \leq 3$;
- (c) Z is selected from the group consisting of a hydroxyl, a halogen, and mixtures thereof, and $0 < d \leq 6$;

wherein A, M, Z, a, b and d are selected so as to maintain electroneutrality of the electrode active material.

102 (PREVIOUSLY PRESENTED): The electrode active material according to Claim 101, wherein A is Li.

103 (PREVIOUSLY PRESENTED): The electrode active material according to Claim 101, wherein A is selected from the group consisting of Li, Na, and mixtures thereof.

104 (PREVIOUSLY PRESENTED): The electrode active material according to Claim 101, wherein a is 0.1 to about 6.

105 (PREVIOUSLY PRESENTED): The electrode active material according to Claim 101, wherein a is from about 2 to about 6.

106 (PREVIOUSLY PRESENTED): The electrode active material according to Claim 101, wherein a is from about 3 to about 6.

107 (PREVIOUSLY PRESENTED): The electrode active material according to Claim 101, wherein M comprises a transition metal selected from Groups 4 through 11 of the Periodic Table.

108 (PREVIOUSLY PRESENTED): The electrode active material according to Claim 107, wherein M is a +3 oxidation state transition metal selected from Groups 4 through 11 of the Periodic Table.

109 (PREVIOUSLY PRESENTED): The electrode active material according to
Claim 107, wherein M is selected from the group consisting of Fe, Co, Ni, Mn, Cu, V, Zr,
Ti, Cr, and mixtures thereof.

110 (PREVIOUSLY PRESENTED): The electrode active material according to
Claim 101, wherein M is M'M'', wherein M' is at least one transition metal selected from
Groups 4 through 11 of the Periodic Table, and M'' is at least one element selected from
Groups 2, 3, 12, 13, and 14 of the Periodic Table.

111 (PREVIOUSLY PRESENTED): The electrode active material according to
Claim 110, wherein M' is selected from the group consisting of Fe, Co, Ni, Mn, Cu, V,
Zr, Ti, Cr, and mixtures thereof.

112 (PREVIOUSLY PRESENTED): The electrode active material according to
Claim 111, wherein M' is selected from the group consisting of Fe, Co, Mn, Cu, V, Cr,
and mixtures thereof.

113 (PREVIOUSLY PRESENTED): The electrode active material according to
Claim 111, wherein M'' is selected from the group consisting of Mg, Ca, Zn, Sr, Pb, Cd,
Sn, Ba, Be, Al, and mixtures thereof.

114 (PREVIOUSLY PRESENTED): The electrode active material according to
Claim 113, wherein M" is selected from the group consisting of Mg, Ca, Zn, Ba, Al, and
mixtures thereof.

115 (PREVIOUSLY PRESENTED): The electrode active material according to
Claim 110, wherein M' is selected from the group consisting of Mg, Ca, Zn, Sr, Pb, Cd,
Sn, Ba, Be, Al, and mixtures thereof.

116 (PREVIOUSLY PRESENTED): The electrode active material according to
Claim 101, wherein M consists of a transition metal selected from Groups 4 through 11
of the Periodic Table.

117 (PREVIOUSLY PRESENTED): The electrode active material according to
Claim 101, wherein Z comprises F.

118 (PREVIOUSLY PRESENTED): The electrode active material according to
Claim 101, wherein Z is F.

119 (PREVIOUSLY PRESENTED): The electrode active material according to
Claim 101, wherein Z is selected from the group consisting of OH, F, Cl, Br, and
mixtures thereof.

120 (PREVIOUSLY PRESENTED): The electrode active material according to
Claim 101, wherein M is V, and Z is F.

121 (PREVIOUSLY PRESENTED): The electrode active material according to
Claim 101, wherein Z comprises OH.

122 (PREVIOUSLY PRESENTED): The electrode active material according to
Claim 101, wherein Z is OH.

123 (PREVIOUSLY PRESENTED): The electrode active material according to
Claim 101, wherein d is from 0.1 to about 6.

124 (PREVIOUSLY PRESENTED): The electrode active material according to
Claim 101, wherein d is from about 2 to about 6

125 (PREVIOUSLY PRESENTED): The electrode active material according to
Claim 101, wherein d is from about 3 to about 6.

126 (PREVIOUSLY PRESENTED): A battery, comprising:

a first electrode comprising electrode active material represented by the general formula:



wherein,

- (a) A is selected from the group consisting of Li, Na, K, and mixtures thereof, and $0 < a \leq 8$;
- (b) M comprises one or more metals, wherein at least one of the one or more metals is capable of undergoing oxidation to a higher valence state, and $1 \leq b \leq 3$;
- (c) Z is selected from the group consisting of a hydroxyl, a halogen, and mixtures thereof, and $0 < d \leq 6$; wherein A, M, Z, a, b and d are selected so as to maintain electroneutrality of the electrode active material.

the battery further comprising a second electrode which is a counter-electrode to the first electrode; and
an electrolyte.

127 (PREVIOUSLY PRESENTED): The battery according to Claim 126, wherein A is Li.

128 (PREVIOUSLY PRESENTED): The battery according to Claim 126, wherein A is selected from the group consisting of Li, Na, and mixtures thereof.

129 (PREVIOUSLY PRESENTED): The battery according to Claim 126, wherein a is 0.1 to about 6.

130 (PREVIOUSLY PRESENTED): The battery according to Claim 126, wherein a is from about 2 to about 6.

131 (PREVIOUSLY PRESENTED): The battery according to Claim 126, wherein a is from about 3 to about 6.

132 (PREVIOUSLY PRESENTED): The battery according to Claim 126, wherein M comprises a transition metal selected from Groups 4 through 11 of the Periodic Table.

133 (PREVIOUSLY PRESENTED): The battery according to Claim 132, wherein M is a +3 oxidation state transition metal selected from Groups 4 through 11 of the Periodic Table.

134 (PREVIOUSLY PRESENTED): The battery according to Claim 132, wherein M is selected from the group consisting of Fe, Co, Ni, Mn, Cu, V, Zr, Ti, Cr, and mixtures thereof.

135 (PREVIOUSLY PRESENTED): The battery according to Claim 126, wherein M is M'M'', wherein M' is at least one transition metal selected from Groups 4 through 11 of the Periodic Table; and M'' is at least one element selected from Groups 2, 3, 12, 13, and 14 of the Periodic Table.

136 (PREVIOUSLY PRESENTED): The battery according to Claim 135, wherein M' is selected from the group consisting of Fe, Co, Ni, Mn, Cu, V, Zr, Ti, Cr, and mixtures thereof.

137 (PREVIOUSLY PRESENTED): The battery according to Claim 136, wherein M' is selected from the group consisting of Fe, Co, Mn, Cu, V, Cr, and mixtures thereof.

138 (PREVIOUSLY PRESENTED): The battery according to Claim 136, wherein M'' is selected from the group consisting of Mg, Ca, Zn, Sr, Pb, Cd, Sn, Ba, Be, Al, and mixtures thereof.

139 (PREVIOUSLY PRESENTED): The battery according to Claim 138, wherein M" is selected from the group consisting of Mg, Ca, Zn, Ba, Al, and mixtures thereof.

140 (PREVIOUSLY PRESENTED): The battery according to Claim 135, wherein M" is selected from the group consisting of Mg, Ca, Zn, Sr, Pb, Cd, Sn, Ba, Be, Al, and mixtures thereof.

141 (PREVIOUSLY PRESENTED): The battery according to Claim 126, wherein M consists of a transition metal selected from Groups 4 through 11 of the Periodic Table.

142 (PREVIOUSLY PRESENTED): The battery according to Claim 126, wherein Z comprises F.

143 (PREVIOUSLY PRESENTED): The battery according to Claim 126, wherein Z is F.

144 (PREVIOUSLY PRESENTED): The battery according to Claim 126, wherein Z is selected from the group consisting of OH, F, Cl, Br, and mixtures thereof.

145 (PREVIOUSLY PRESENTED): The battery according to Claim 126, wherein M is V, and Z is F.

146 (PREVIOUSLY PRESENTED): The battery according to Claim 126, wherein Z comprises OH.

147 (PREVIOUSLY PRESENTED): The battery according to Claim 126, wherein Z is OH.

148 (PREVIOUSLY PRESENTED): The battery according to Claim 126, wherein d is from 0.1 to about 6.

149 (PREVIOUSLY PRESENTED): The battery according to Claim 126, wherein d is from about 2 to about 6

150 (PREVIOUSLY PRESENTED): The battery according to Claim 126, wherein d is from about 3 to about 6.

151 (PREVIOUSLY PRESENTED): The battery according to Claim 126, wherein the second electrode comprises a material selected from the group consisting of a metal oxide, metal chalcogenide, carbon, graphite, and mixtures thereof.

152 (PREVIOUSLY PRESENTED): The battery according to Claim 151, wherein the electrolyte comprises a solvent selected from the group consisting of dimethyl carbonate, diethyl carbonate, dipropylcarbonate, ethyl methyl carbonate, butylene carbonate, γ -butyrolactone, triglyme, tetraglyme, a lactone, an ester, dimethylsulfoxide, dioxolane, sulfolane, and mixtures thereof.

153 (PREVIOUSLY PRESENTED): The battery according to Claim 152, wherein the electrolyte further comprises a lithium salt selected from the group consisting of LiAsF₆, LiPF₆, LiClO₄, LiB(C₆H₅)₄, LiAlCl₄, LiBr, and mixtures thereof.

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PRIOR-ART APPENDIX

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HYDROTHERMAL SYNTHESIS OF $MTi_2(PO_4)_3$ (M=Li,Na,K)

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ABSTRACT

$MTi_2(PO_4)_3$ (M=Li,Na,K) compounds and corresponding single-crystals have been obtained from MOH , TiO_2 and 85% H_3PO_4 by hydrothermal crystallization. The conditions of the crystallization and crystal growth were described. X-ray, Raman and ^{31}P MAS NMR studies were performed on these compounds to understand the characterization and purity of the products. The advantages of the hydrothermal crystallization compared with the solid state reaction for preparing $MTi_2(PO_4)_3$ compounds were discussed.

MATERIALS INDEX: titanium, lithium, triphosphates, NASICON.

Introduction

There is considerable interest in study on ionic conductors recently, particularly after the development of NASICON(1), with a three-dimensional network of PO_4 and SiO_4 tetrahedra corner-shared with ZrO_4 octahedra. The $MTi_2(PO_4)_3$ compounds have a NASICON-type structure (space group $R\bar{3}c$) in which the structure consists of PO_4 tetrahedra and TiO_6 octahedra linked by the corners(2). These materials have a property of ionic conduction. One of them, $LiTi_2(PO_4)_3$, exhibits high lithium ion conduction(2,3). Since Ti^{4+} ion has a smaller size than Zr^{4+} , it can be thus expected that $MTi_2(PO_4)_3$ may be possibly a good host compounds for ion substitution(4).

All these compounds were prepared by high temperature solid state reactions(2,5). Like NASICON compounds, there have been some problems in the preparation of $MTi_2(PO_4)_3$ compounds, such as the difficulty for the synthesis; lack of stoichiometry in final products; lack of single crystals (the products from solid state reaction are mostly twinned). Therefore, it becomes very important to search for a new convenient synthetic method of the NASICON-type compounds for overcoming the difficulty mentioned above. In recent years, the hydrothermal method has been developed for the synthesis of phosphate ionic conductors, owing to the low PT-conditions for crystalliza-

tion(6).

In this paper, a new method, hydrothermal crystallization for synthesizing $M\text{Ti}_2(\text{PO}_4)_3$ compounds, and characterization of the products were reported.

Experimental

The hydrothermal crystallization was carried out in Teflon-lined autoclaves for obtaining $M\text{Ti}_2(\text{PO}_4)_3$ compounds. TiO_2 (anatase), 85% H_3PO_4 and alkaline metal hydroxides were employed as the starting materials. The alkaline solutions with a definite concentration act as a mineralizer. The starting materials were mixed in the definite molar ratio in the Teflon liner. The autoclaves were sealed and heated in an oven at 200-250 °C for 5-7 days. The products were recovered by filtering, washing and drying.

The phase of the products was identified by X-ray powder diffraction using a Rigaku D/MAX-III A diffractometer with $\text{Cu}-\text{k}\alpha$ ($\lambda = 1.5418$) radiation. Raman spectra were recorded on a Ramanor SPEX 1403 double spectrometer using an argon-ion laser with 488.0 nm line at 100mw. ^{31}P MAS NMR spectra were acquired on a Varian XL-200 spectrometer at 80.96 MHz. The chemical shifts are referred to 85% H_3PO_4 .

Results and Discussions

A large number of batches were carried out by changing the temperature and the molarity of the alkaline solutions in a definite ranges, in order to obtain the pure products. The experimental results show that pure $\text{LiTi}_2(\text{PO}_4)_3$, $\text{NaTi}_2(\text{PO}_4)_3$, and $\text{KTi}_2(\text{PO}_4)_3$, can be obtained from the hydrothermal crystallization system respectively, and that pH values of systems and temperature are the critical factors for crystallization. The optimum crystalline conditions hydrothermally for $M\text{Ti}_2(\text{PO}_4)_3$ compounds are as follows.

The molar ratio of the starting materials:

(3.5-4.5)M₂O:(0.3-0.5)TiO₂:(12-15)P₂O₅, (M=Li, Na, K)

Temperature of crystallization: 250°C

Time of crystallization: 5-7 days

Alkaline solution concentration: 1.5-2M.

In usual case, the products are fine white powder. The growth of phosphates by the hydrothermal technique is relatively new. In general, there are very few reports on the growth of phosphates by this method(7,8). Therefore, a attempt to grow triphosphates by the hydrothermal technique have been made. Since most of phosphates show a negative temperature coefficient of solubility under hydrothermal conditions, the temperature of the oven was slowly raised up to a predetermined temperature to obtain good crystals. Here the rate of heating was the main parameter to reduce the number of crystals and increase the size of the crystals. The cube-shaped crystals of $\text{LiTi}_2(\text{PO}_4)_3$, $\text{NaTi}_2(\text{PO}_4)_3$, and $\text{KTi}_2(\text{PO}_4)_3$, were obtained under the above conditions, which have the sizes of 100 μm , 70 μm , and 50 μm respectively.

The X-ray powder diffraction patterns of the products were studied to identify the purity of the phases. These patterns were identical to the ones published respectively(2,9), and showed that these products are with a good crystallinity and free of TiO_2 and other impurities.

The Raman spectra of $M\text{Ti}_2(\text{PO}_4)_3$ are shown in Figure 1. These spectra are unique and quite characteristic of triphosphates, with a sharp peak at 1010 cm^{-1} , and other Raman bands of each compound are different because of

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tion for synthesis-
ducts were repor-

eflon-lined autoclave. 85% H_3PO_4 and alkali. The alkali was added to the Teflon liner. 0 °C for 5-7 days. After diffraction. 0.5418) radiation. Double spectrometer

spectrometer at

5000
10000

the temperature ranges, in order to obtain pure $LiTi_2(PO_4)_3$ from the hydrothermal systems and to obtain optimum crystalline as follows.

The growth of phosphate. In general, there is a method(7,8). These techniques have been re-coefficient of the oven was good crystals. the number of crys-
ped crystals of $LiTi_2(PO_4)_3$ in the above condi-
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TRIPHOSPHATES

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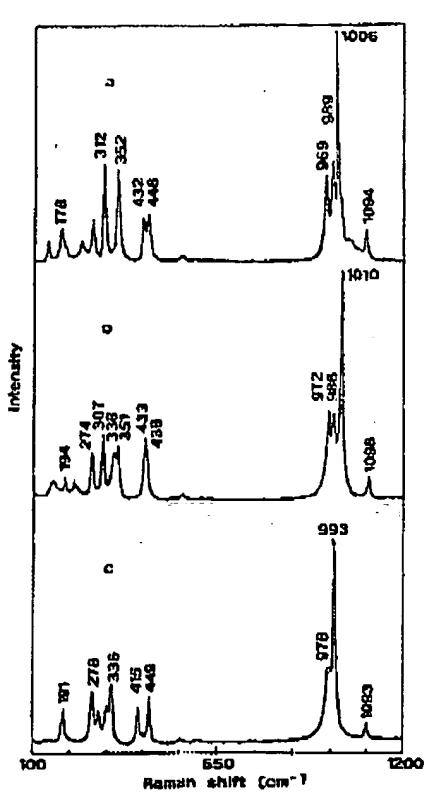


FIG. 1

The Raman spectra of $MTi_2(PO_4)_3$.
a. $LiTi_2(PO_4)_3$;
b. $NaTi_2(PO_4)_3$;
c. $kTi_2(PO_4)_3$.

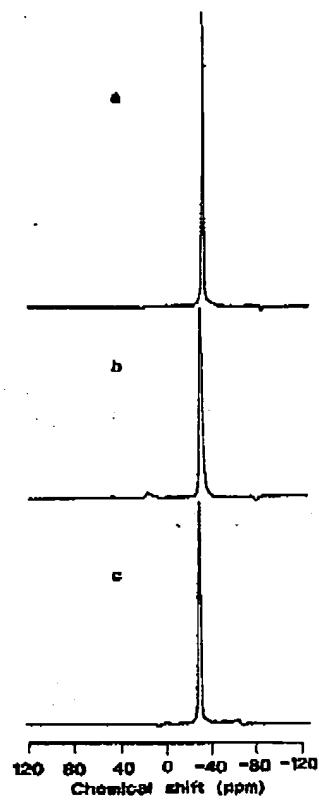


FIG. 2

80.9MHz ^{31}P MAS NMR spectra of $MTi_2(PO_4)_3$.
a. $LiTi_2(PO_4)_3$;
b. $NaTi_2(PO_4)_3$;
c. $kTi_2(PO_4)_3$.

the difference of M^{+} cations. From the Raman spectra it was found that in the final products there were no $M(TiO)PO_4$ and $M(TiO)(PO_4)_2$ compounds which their characteristic peaks of the Raman spectra were 745cm^{-1} and 687cm^{-1} respectively(10).

An important feature of the hydrothermal synthesis of $MTi_2(PO_4)_3$, was that the resultant products were highly homogeneous in composition with only

(P_2O_{12}) radical group. On contrary, most of high temperature solid state reactions and flux methods always resulted in the formation of a few other radicals like (P_2O_7), (P_3O_6), (P_4O_{10}) and (P_5O_{10}) etc. in the final products (6). The absence of these condensed radicals was confirmed through ^{31}P NMR spectra of the products. Each compound has only single ^{31}P resonance line -27.5 ppm (Figure 2) as expected from the space group $R\bar{3}c$, since the phosphorus in these compounds are crystallographically equivalent(11).

These materials heated up to 1200°C in air were stable and no melting occurred. We think that these materials have identical properties with specimens prepared by other methods. The chemical and physical properties on these compounds will be investigated further and published elsewhere.

Conclusions

Hydrothermal method is superior to solid state reaction for synthesizing $MTi_2(PO_4)_3$. The compounds of $MTi_2(PO_4)_3$ and corresponding single crystals can be obtained in low PT-conditions of crystallization. The results of XRD, Raman and ^{31}P NMR studies confirm that the products are with a good crystallinity, free of TiO_2 and the impurities of other condensed phosphates. This study suggests the possibility to prepare pure NASICON phases hydrothermally.

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